91-e14

Basic Water Monitoring Program Fish Tissue and Sediment Sampling for 1989

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ABSTRACT

As part of the 1989 Basic Water Monitoring Program, fish tissue or sediment samples were collected at nine river locations in Washington State. The level of chemical contamination found at these locations was typically low, in most cases at or near the analytical detection limit. The only notable exception were DDT compounds (DDT and metabolites) found in the Walla Walla River tissue samples. The concentration of total DDT compounds in the Walla Walla sample, when expressed on a lipid weighted basis, was in the range of concentrations reported in whole fish samples from the lower Yakima River. The Walla Walla River should be considered for further investigations.

INTRODUCTION

As part of Washington's Basic Water Monitoring Program (BWMP), the Ambient Monitoring Section of the Washington State Department of Ecology collects fish tissue samples from selected sites throughout the state. Fish tissue composites from these locations are analyzed for selected metals and organic compounds. The data generated by the program is used to identify potentially contaminated locations requiring further investigations. Examples of BWMP data triggering large intensive investigation include DDT in Yakima River fish and elevated heavy metals in the upper Columbia.

Survey Plan

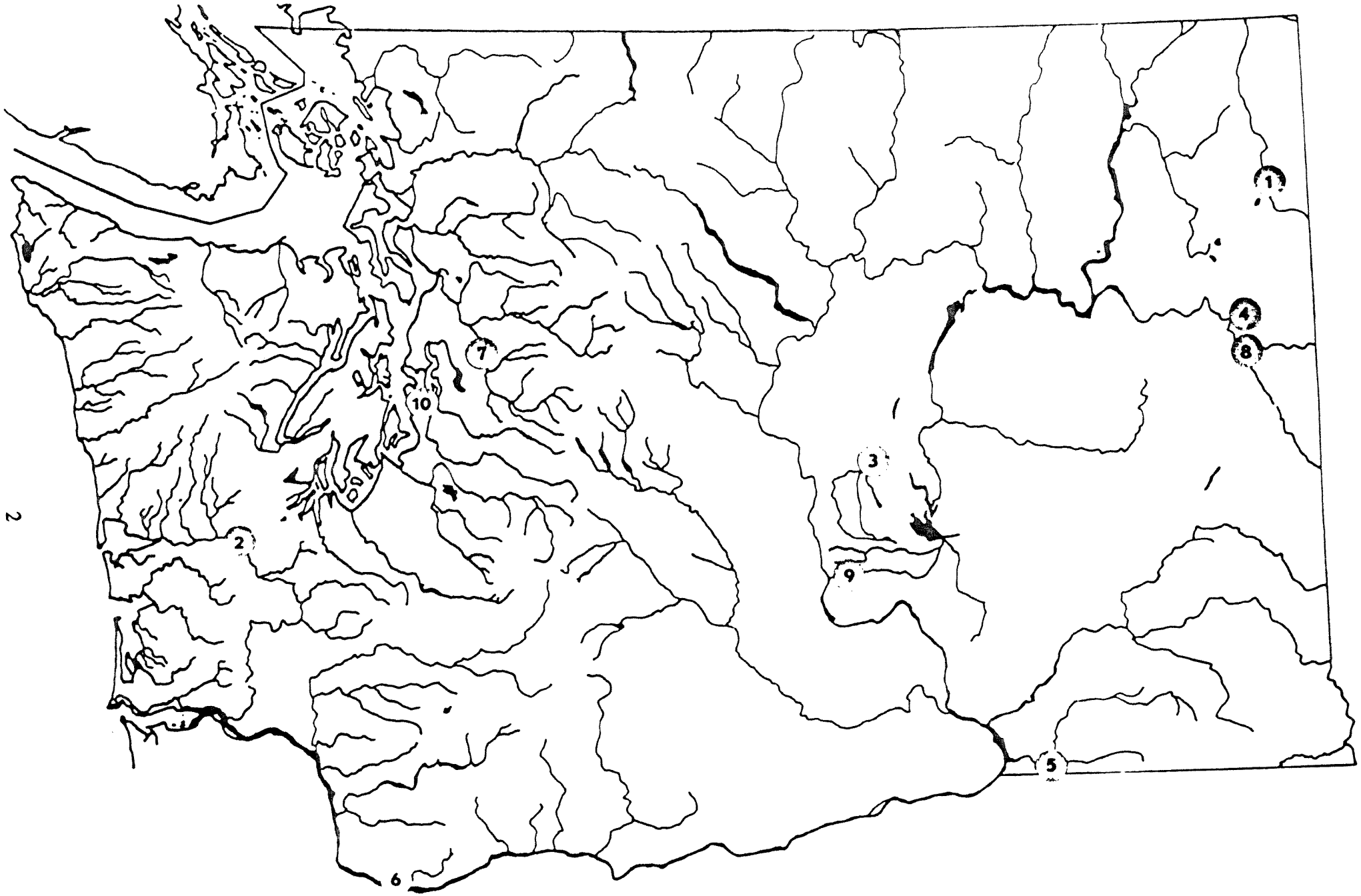
Ten locations were selected for sampling based on the recommendations from the regional office staff of Ecology and the Department of Wildlife. They are listed below:

Station Name

1. Pend Oreille River at Usk.
2. Chehalis River at Porter.
3. Winchester Wasteway near Interstate Highway 90.
4. Little Spokane River near mouth.
5. Walla Walla River below Warm Springs near Touchet.
6. Columbia River near Camas.
7. Snoqualmie River near Carnation.
8. Spokane River below Riverside State Park.
9. Crab Creek near Beverly.
10. Green/Duwamish River near Allentown.

These ten locations are shown in Figure 1. For specific information on exact sample location, see Appendix 1.

Figure 1. Sample Locations for the 1989 BWMP Sampling Program.



Sampling was conducted during May-June and in August-September 1989. At each location, an attempt was made to collect a grazer species and a game fish species. The target grazer was a sucker (*Catostomus sp.*) and the game fish was a resident salmonid (*Oncorhynchus sp.*) or bass (*Micropterus sp.*). The sucker species was processed as a whole fish sample and the game species was filleted (skin on). If no resident game or grazer species was collected during either the spring or fall sampling, a sediment sample was collected. The exception to this was at the Green/Duwamish. No sediment sample was collected on the Green River due in part to difficulty encountered in collecting a representative sediment sample during the 1984 BWMP sampling effort.

METHODS

Spring Sampling

The spring sampling effort was hindered by high flows and poor water visibility. After expending over 100 man-hours in the field with limited success at only one location (Chehalis River), the spring sampling was terminated.

Fall Sampling

The fall sampling effort was successful at only two locations and had limited success at four others. No fish were collected at Crab Creek, Spokane River, and the Green/Duwamish River. Sediment samples were substituted for fish tissue at Crab Creek and Spokane River.

Fish Tissue

Sample Collection and Handling

Fish samples were collected using a Model SR-16 Smith-Root electroshocking boat or a type VII backpack unit. Upon collection, the samples were wrapped in aluminum foil (dull side in) and placed in a plastic bag. Samples were held on ice until they could be frozen. Length (cm) and weight (gm) measurement for each individual in the composite are reported in Table 1.

The grazer species were placed on aluminum foil (dull side up) and cut into pieces that could be processed through a Horbart commercial meat grinder. All dissecting utensils and the meat grinder were cleaned with Liquinox (a laboratory grade non-phosphate detergent), and rinsed three times each with deionized water, two percent nitric acid and pesticide grade acetone. Upon completion of compositing, the samples were split into two commercially prepared glass containers (I-Chem), one for metals analysis and the other for pesticide/PCB determination. The game species were filleted, ground, and composited as above.

Sediment

An attempt was made to collect sediment from a depositional area, behind bridge piers/slack water areas, were possible. Sediment was collected with a six-inch stainless steel ponar grab washed with Liquinox and rinsed three times each with deionized water, two percent nitric acid and pesticide grade acetone. The top 2 cm of at least five individual samples were transferred to a stainless steel beaker, homogenized, and placed in I-Chem glass containers (for metals and organic analysis) and a plastic Whirl pac (for grain size determinations).

At the Crab Creek location, compositing of the top 2 cm was not practical due to the hard substrate and lack of sediment depositional areas. Therefore, all fine grained sediment in the ponar, after removing the larger debris and gravel, was used for compositing.

All samples were stored on ice until returned to the laboratory. Samples for organic and metals determination were frozen pending analysis, and those for total organic carbon and grain size analysis were held at 4°C.

Sample Analysis

Organics

The organic compounds selected for analysis and the target detection limits are presented in Table 2. These compounds were selected after reviewing the list of analtyes from the following studies, EPA's National Bioaccumulation Study (Terpening, 1987), California's Toxic Substance Monitoring Program (Agee, 1986), U.S. Fish and Wildlife's National Pesticide Monitoring (Schmitt *et al.*, 1985), and historical BWMP data (Hopkins *et al.*, 1985).

Sample analysis followed those procedures presented in Recommended Protocols for Measuring Organic Compounds in Puget Sound Sediment and Tissue Samples (Tetra Tech and Battelle, 1988a). Weyerhaeuser Analytical and Testing Services Analytical Chemistry Laboratories, Tacoma, Washington, provided the analytical services.

Metals

The metals selected for analysis and the required detection limits are reported in Table 2. Selenium and mercury were analyzed in fillet only because these two metals tend to accumulate in axial muscle (Schmitt, C.S. and S.E. Finger, 1987). Analytical Resources Incorporated, Seattle, Washington, completed the metals analysis following those procedures presented in Recommended Protocols for Measuring Metals in Puget Sound Water, Sediment, and Tissue Samples (PSEP, 1988b).

Quality Assurance/Quality Control (QA/QC)

The QA/QC required in this study was as follows:

	Type of QA/QC	Number of Samples	Sample Type
1)	Field Replicates	1	F
2)	Blind Laboratory Replicates (after processing)	2	F
3)	Matrix Spike	1	F,S
4)	Matrix Spike Duplicate	1	F,S
5)	Standard Reference Material		
	a) Pesticides (EPA)	1	F
	b) Metals (DORM-1)	1	F
	c) Buffalo River Sediment	1	S
6)	Method Blanks	1	F,S
7)	Surrogate Recovery (pesticide only)	1	F,S

F= Fish Tissue S= Sediment

Results from these QA/QC tests were compared with ranges provided in Puget Sound Protocols (Tetra Tech and Battelle 1988a and 1988b). Data was qualified for QA/QC results outside the required ranges. The individual QA/QC results and corresponding discussion are provided in Appendices 2-5.

RESULTS AND DISCUSSION

Organics

Fish Tissue

The results for the organics compounds in the fish tissue composites are presented in Table 3. Organic compounds listed in Table 2 and not found in Table 3 were analyzed for, but not detected.

In most cases the compounds, if detected, were near the detection limits. The only exceptions were aldrin, dieldrin, DDT and its metabolites DDD and DDE. Aldrin and dieldrin was detected in samples from Winchester Wasteway and the Columbia River at Camas. The aldrin results were low (near detection limits) and may or may not be valid due to the detection of aldrin in the laboratory blank (B qualifier code) see Appendix 2. Dieldrin level at both locations

are elevated, 37 ug/Kg for Winchester Wasteway and 40 ug/Kg for Columbia River, but are well below the 100 ug/Kg wet weight for whole fish and the National Academy of Science (NAS) suggested for the protection of predators (NAS, 1973).

DDT and its metabolites were found in the Walla Walla River and the Winchester Wasteway. The 527 ug/Kg wet weight total DDT forms (t-DDT=DDT+DDD+ DDE) found in the Walla Walla River are considered elevated. This level is higher than 46% of the results reported in whole fish collected from the Yakima River, a river with known elevated DDT compounds (Johnson *et al.*, 1986); the range of t-DDT results in Johnson's Yakima River study was 50-3000 ug/Kg wet weight. When the results are normalized to percent lipid, the concentration found in the Walla Walla sample (13,863 lipid normalized) is higher that 69% of those found in the Yakima River. The Winchester Wasteway composite shows the presence of DDT metabolites, but they were at levels much lower than those found in the Walla Walla composite (197 ug/Kg t-DDT and 5,179 lipid normalized vs. 527 ug/Kg and 13,863 lipid normalized). Both of these locations, though somewhat elevated, are well below the National Academy of Science total body burden of DDT, and it metabolites of 1000 ug/Kg wet weight in whole fish. The large contribution of the DDE metabolite to the t-DDT forms indicates that for both of these rivers, historical applications appear to be the cause of the elevated t-DDT.

Sediment

The results for pesticides, base/neutral acid, herbicides, and the corresponding QA are presented in Appendix 3. The results for grain size determination are given in Table 4.

All organic compounds analyzed for were below detection limits. The high percentage of gravel and sand in the grain size determinations, 93% average for Crab Creek and 76% for Spokane River samples, indicates that less than ideal sediment samples were collected. Organics are normally associated with the silt and clay fraction, and the limited quantity of these two fractions may have contributed to the low level evident here.

Metals

Fish Tissue

The levels of metal found in the fish tissue composites are reported in Table 5. QA/QC results are present and reviewed in Appendix 4. As a point of reference for the 1989 BWMP metals results, Table 6 provides a summary of the most recent USFWS National Contamination Biomonitoring Program (NCBP) metals results on a national scale (Lowe *et al.*, 1985).

1989 BWMP Results vs. USFWS NCBP

Table 7 shows 1989 BWMP data that exceeds the NCBP national 85th percentile metal levels.

Zinc and Copper

Zinc and copper are essential trace elements (Mertz, 1981) and are not always associated with elevated concentrations in water (Schmitt, 1987). Potentially elevated zinc and copper concentrations found in the 1989 BWMP may be less of a concern than elevated levels of other non-essential trace metals, specifically cadmium, lead, and mercury.

Cadmium

Cadmium concentrations in three of the seven rivers tested as part of the 1989 BWMP exceeded the NCBP 85th Percentile. These rivers, though elevated, all had concentrations significantly less than the 2000 ug/Kg wet weight level believed to indicate probable cadmium contamination (Eisler, 1985).

Lead

Lead concentrations exceeded the NCBP 85th percentile on the Little Spokane River. This lead concentration was, however, qualified as estimates and should be used with care.

Mercury (Fillet Only)

Though the mercury results for the Pend Oreille fillet showed possibly elevated levels of mercury, it does not exceed the NCBP 85th percentile, 120 ug/Kg ppm compared to 180 mg/Kg or the NAS standard of 500 ug/Kg wet weight (NAS, 1973). The small size of the fish collected on the Pend Oreille (see Table 1) indicate their age to be 1-2 years old (Scott and Crossman, 1973). Mercury is commonly believed to accumulate as methylmercury in the muscle of fish and tends to increase with age (Tollefson and Cordle, 1986). Therefore, older fish in the Pend Oreille River may exceed the NCBP 85th percentile. The mercury results for the Pend Oreille were, however, qualified by the laboratory as an estimate.

Selenium (Fillet Only)

The Winchester Wasteway had a selenium level of 350 ug/Kg ppm wet weight in the fillet. This concentration is below the USFWS national geometric mean of 470 ug/Kg, wet weight.

Sediment Metals

The results for the sediment sample collected on Crab Creek and the Spokane River are presented in Table 8. QA/QC results are presented and reviewed in Appendix 5. For comparison Table 9 presents the 95th, 75th and median for metals in freshwater sediment collected in Washington State as part of the 1984 BWMP (Hopkins *et al.*, 1985) and the 1989 Lakes and Reservoir Water Quality Assessment Program (Johnson, 1990).

The sediment collected on the Spokane River exceeds the 75th percentile for arsenic, cadmium, lead, and zinc. The Crab Creek sediment sample is below the median for the six metals listed in Table 9, except for arsenic, which is questionable because of QA\QC problems.

CONCLUSIONS

With the exception of few organic pesticides in fish samples all of the organic compounds analyzed for, in both sediment and tissue samples, were below detection limits. DDT/metabolites were found in Walla Walla River and Winchester Wasteway. Aldrin and dieldrin were detected in the Winchester Wasteway and the Columbia River at Camas tissue samples. Some of these results appear elevated but all were substantially below NAS standards.

Metals concentration in fish tissue, though slightly elevated in some cases, for the most part do not appear to be a problem in those areas sampled. The one exception to this may be the level of mercury found in the Pend Oreille River sample. The results were qualified by the laboratory as an estimate and should be verified by a follow up study.

Sediment samples, though of limited usefulness for organic analysis, did indicate metal problems on the Spokane River.

RECOMMENDATIONS

1. The high number of less than detected values indicates the current BWMP list of organic pesticides, most of which are no longer applied or highly regulated, should be updated to reflect pesticides and other organic compounds of current concern. One possible starting point for the development of a new list would be Pesticides of Concern in the Puget Sound Basin: A Review of Contemporary Pesticide Usage, prepared by Tetra Tech for U.S. Environmental Protection Agency Region X, September 1988. However, as the above report states, many of the currently used pesticides do not have analytical protocols readily available for environmental samples.

2. The low level of fine sediment associated with the samples collected from the Spokane River and Crab Creek reflects the ineffectiveness of the collecting method in this type of stream environment. Both locations were relatively fast moving with no discernible depositional area for sediment collection. A review of the current methods of collecting freshwater sediment in a typical Washington river or stream (that is, steep gradient, fast moving and with a seasonally scoured bottom) should be conducted. Possible methods that should be evaluated are sediment traps and flow through centrifugation.

3. Walla Walla River should be considered for a more indepth investigation of the DDT contamination.

4. Larger fish should be collected from the Pend Oreille River to confirm or refute the possibly elevated mercury levels.

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TABLES

Table 2. Target chemicals/metals and corresponding detection limits for Ecology's 1989 BWMP fish tissue monitoring.

Organic Compounds	Detection limits (ug/kg wet weight)
aldrin	8
chlordane (cis and trans)	80
dieldrin	16
DDT and metabolites	16
endosulfan I	8
endosulfan II	16
endosulfan sulfate	16
endrin	16
endrin aldehyde	80
heptachlor	8
heptachlor epoxide	8
alpha BHC	8
beta BHC	8
gamma BHC (Lindane)	8
delta BHC	8
toxaphene	160
methoxychlor	80
Aroclor - 1016	80
Aroclor - 1221	80
Aroclor - 1232	80
Aroclor - 1242	80
Aroclor - 1248	80
Aroclor - 1254	160
Aroclor - 1260	160
nonachlor (cis and trans)	16
oxychlordane	80
hexachlorobenzene	8
mirex	80
DCPA	80
Tetradifon	8

Metals	Sample Type	Detection limit (ug/kg wet weight)
selenium	F	200
mercury	F	100
arsenic	F,W	300
cadmium	F,W	500
copper	F,W	600
chromium	F,W	1000
lead	F,W	200
zinc	F,W	1000

F= Fillet W= Whole

Table 4. Grain size results in table are percent for the 1989 BWMP sediment composites.

Station Location	Date	Percent Gravel	Sand	Silt	Clay
Crab Creek at Beverly	1/18/90	10	78	10	2
Duplicate		10	88	<1	2
Spokane River Below Riverside State Park	1/18/90	13	61	21	4

Gravel = >2mm
Sand = 2mm-62um
Silt = 62um-4um
Clay = <4um

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Table 6. Summary data from the USFWS National Contamination Biomonitoring Program on metals concentrations in whole fish (Lowe, *et al.*, 1985).

		Metals Concentration (ug/Kg, wet weight; ppb)						
Location		Zn	Cu	Pb	As	Cd	Hg	Se
U.S. Freshwater	mean	23800	680	170	140	30	110	47
(112 Stations	85th	40100	900	250	220	60	180	710
Nation-wide)	maximum	109000	24100	1940	1700	350	770	2470
1980-1981								

Table 7. 1989 BWMP largescale sucker metals data that equals or exceeds 1980 USFWS National Contamination Biomonitoring Program 85th percentile.

Station	Zn	Cu*	As	Cd
Little Spokane River	**			**
Snoqualmie River		**		**
Columbia River				
Pend Oreille River				**
Chehalis River				
Winchester Wasteway				
Walla Walla River				

* Blank corrected.

** Equals or exceeds 1980 USFWS NCBP 85th percentile.

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Columbia River				
Pend Oreille River				**
Chehalis River				
Winchester Wasteway				
Walla Walla River				

* Blank corrected.

** Equals or exceeds 1980 USFWS NCBP 85th percentile.

Table 8. Metals results (ug/Kg, dry weight) for the 1989 BWMP sediment composites.

Station Location	Date	Percent TOC	Percent Solids	Al	Sb	As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Se	Ag	Tl	Zn
Crab Creek at Beverly	1/18/90	36	68.6	8540000J	100J	6860	300	120	8700J	8400	9700	60U	7000	700	40	200J	27600
Spokane River Below Riverside State Park	1/18/90	72	80.6	13100000J	900J	11700	4000	1590	15400J	12900	51000	30	11000	530	170	200J	275000

NA - Not analyzed.
J - Estimated

Table 9. The 95th percentile, 75th percentile, and median for metals in freshwater sediment collected in Washington State as part of the 1984 BWMP and the 1989 Lakes and Reservoir Water Quality Assessment Program (ug/Kg, dry weight; ppb).

	As	Cd	Cr	Cu	Pb	Zn
95th Percentile	20100	8300	199000	172000	196000	946000
75th Percentile	9400	1000	58300	52900	30300	112800
Median	580	460	21200	37100	13100	68000

N=28

APPENDICES

Appendix 1. Sample site descriptions for the 1989 BWMP fish tissue and sediment collection.

Pend Oreille at Usk - Near the Usk Bridge over the Pend Oreille River.

Chehalis River at Porter - From ¼ mile upstream to ¼ mile downstream of the bridge crossing the Chehalis River at Porter.

Winchester Wasteway near I-90 - At south end of pool, north of I-90.

Little Spokane River Near Mouth - Below Highway 291 bridge north of Spokane.

Walla Walla River below Warm Springs near Touchet - Below the Cummings Road Bridge.

Columbia River near Camas - North bank ½ mile below Lady Island to West end of Lady Island.

Snoqualmie River near Carnation - From 2 to 2½ miles upstream of the City of Carnation (near golf course).

Spokane River below Riverside State Park - From Seven Mile Bridge to 1/2 mile below Riverside State Park. Sediment sample was collected near the east bank at Seven Mile Bridge.

Crab Creek at Beverly - Above and below Crab Creek Road Bridge. Sediment sample was collected below bridge.

Green/Duwamish River near Allentown - From the Allentown Bridge over the Green Duwamish, to ½ mile above Foster golf course.

Appendix 2. Quality assurance results and discussion for organic compounds in fish tissue composites collected as part of the 1989 BWMP.

The QA/QC results for the organic compounds were almost all within the required ranges except for aldrin and T-DDE. Aldrin was detected in the method blank and each value reported above the detection limit and less than ten times the level found in the method blank is flagged with a "B" qualifier.

Part A. Laboratory results and acceptable ranges for EPA reference material Pesticides in Fish.

Compound	Laboratory Conc. ug/Kg First Run	Laboratory Conc. ug/Kg Second Run	EPA Reference Range ug/Kg	95% C.I. X+2.18S ug/Kg
alpha-BHC	8 U	80 U	41 ± 22	DL - 89
Aldrin	16 B	80 U	NA	
4,4'-DDE	2900 E	3,500	NA	
o,p-DDE	87	80 U	NA	
T-DDE	2,987 E	3,500	2340 ± 290	1710 - 2970
4,4'-DDD	2,300	2,200	NA	
o,p-DDD	28	80 U	NA	
T-DDD	2,328	2,200	1590 ± 380	760 - 2420
4,4'-DDT	1,100	960	NA	
o,p-DDT	130	80 U	NA	
T-DDT	1,230	960	870 ± 490	DL - 1940
Endrin	110	160 U	120 ± 60	DL - 250
Endosulfan II	100	160 U	NA	
alpha-Chlordane	29 J	39 J	NA	
gamma-Chlordane	42 J	800 U	NA	
Aroclor-1260	530	1600 U	NA	
Mirex	41	80 U	NA	
Hexachlorobenzene	24	80 U	NA	

DL = Detection Limit
NA = Not Available
U = Undetected at stated concentration
B = Value less than 10 X concentration detected in method blank
E = Calculation based on a peak that exceeded the linear range
J = Estimated value

Appendix 2 continued.

Part B. Pesticide surrogate recovery and matrix spike/matrix spike duplicate results for the 1989 BWMP tissue analysis.

Matrix Spike

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	Matrix Sp Conc. (ug/Kg)	Percent Recovery (PR)	PR QC limit (soil)
gamma-BHC (lindane)	150	0	140	93.33	46-127
Heptachlor	150	0	96	64.00	35-130
Aldrin	150	0	123	82.00	34-132
Dieldrin	374	0	211	56.42	31-134
Endrin	374	0	285	76.20	42-139
4,4'-DDT	374	0	360	96.26	23-134

Matrix Spike Duplicate

Compound	Spike Added (ug/Kg)	Matrix Sp Conc. (ug/Kg)	Percent Recovery (PR)	PR QC (soil)	Relative Percent Difference	RPD QC (soil)
gamma-BHC (lindane)	144	150	104.17	46-127	- 10.97	50
Heptachlor	144	98.20	68.19	35-130	- 6.35	31
Aldrin	144	125	86.81	34-132	- 5.69	43
Dieldrin	361	232	64.27	31-134	- 13.01	38
Endrin	361	312	86.43	42-139	- 12.57	45
4,4'-DDT	361	413	114.40	23-134	- 17.23	50

PR = Percent Recovery
RPD = Relative Percent Difference

Appendix 3. Results for pesticides, base/neutral acids, herbicides and the corresponding quality assurance/quality control on sediment samples collected as part of the 1989 BWMP. QA results for sediment organic were all within exceptible ranges.

Part A. Results (ug/Kg) for pesticides and PCB on sediment samples collected as part of the 1989 BWMP.

Compound	Spokane R.	Crab Ck.	MS	MSD
Alpha-BHC	3 U	3 U	3 U	3 U
Beta-BHC	3 U	3 U	3 U	3 U
Delta-BHC	5 U	5 U	5 U	5 U
Gamma-BHC (Lindane)	3 U	3 U	-	-
Heptachlor	3 U	3 U	-	-
Aldrin	3 U	3 U	-	-
Heptachlor Epoxide	3 U	3 U	3 U	3 U
Endosulfan I	3 U	3 U	3 U	3 U
Dieldrin	6 U	6 U	-	-
4,4'-DDE	6 U	6 U	6 U	6 U
Endrin	6 U	6 U	6 U	6 U
Endosulfan II	6 U	6 U	6 U	6 U
4,4'-DDD	6 U	6 U	6 U	6 U
Endosulfan Sulfate	12 U	12 U	12 U	12 U
4,4'-DDT	6 U	6 U	-	-
Methoxychlor	12 U	12 U	12 U	12 U
Endrin Ketone	9 U	9 U	9 U	9 U
Gamma-Chlordane	5 U	5 U	5 U	5 U
Alpha-Chlordane	5 U	5 U	5 U	5 U
Toxaphene	450 U	450 U	450 U	450 U
Aroclor-1242/1016	60 U	60 U	60 U	60 U
Aroclor-1248	60 U	60 U	60 U	60 U
Aroclor-1254	60 U	60 U	60 U	60 U
Aroclor-1260	60 U	60 U	60 U	60 U

MS = Matrix Spike
MSD = Matrix Spike Duplicate

Appendix 3. Continued

Part A1. Pesticide surrogate recoveries and matrix spike/matrix spike duplicate results. (sediment)

Pesticide Surrogate Recovery

Dibutylchlorendate	76%	87%	79%	85%

Matrix Spike

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	MS Conc. (ug/Kg)	MS % Recovery	QC Limits
Lindane	16	0	18	109	46-127
Heptachlor	16	0	19	120	35-130
Aldrin	16	0	14	87	34-132
Dieldrin	40	0	32	78	31-134
Endrin	40	0	38	95	42-139
4,4'-DDT	40	0	28	69	23-134

Matrix Spike Duplicate

Compound	Spike Added (ug/Kg)	MSD Conc. (ug/Kg)	MSD % Recovery	% RPD	QC Limits RPD	Recovery
Lindane	16	18	111	1.8	50	46-127
Heptachlor	16	19	111	7.8	31	35-130
Aldrin	16	14	86	1.2	43	34-132
Dieldrin	40	32	81	3.8	38	31-134
Endrin	40	38	95	0.0	45	42-139
4,4'-DDT	40	28	74	7.0	50	23-134

U - Indicates compound was analyzed for but not detected at the given Detection limit.
MS - Matrix Spike
MSD - Matrix Spike Duplicate
RPD - Relative Percent Difference

Appendix 3. Continued

Part B. Results (ug/Kg) for organophosphorus pesticides in sediment samples collected as part of the 1989 BWMP.

Compound	Spokane R.	Crab Ck.	MS	MSD
Dichlorvos(DDVP)	6.0U	6.0U	-	-
EPTC(Eptam)	5.0U	5.0U	5.0U	5.0U
Mevinphos(Phosdrin)	3.0U	3.0U	3.0U	3.0U
Trifluralin	7.0U	7.0U	7.0U	7.0U
Tebuthiuron	16.0U	16.0U	16.0U	16.0U
Systox(Demeton)	5.0U	5.0U	5.0U	5.0U
Ethoprop(Mocap)	1.0U	1.0U	1.0U	1.0U
Phorate	3.0U	3.0U	3.0U	3.0U
Naled	10.0U	10.0U	10.0U	10.0U
Pronamide	32.0U	32.0U	32.0U	32.0U
Prometon	5.0U	5.0U	5.0U	5.0U
Diazinon	1.0U	1.0U	-	-
Atrazine	3.0U	3.0U	3.0U	3.0U
Simazine	9.0U	9.0U	9.0U	9.0U
Disulfoton(Di-Syston)	1.0U	1.0U	1.0U	1.0U
Ronnel(Fenchlorphos)	3.0U	3.0U	3.0U	3.0U
Methyl Parathion	3.0U	3.0U	3.0U	3.0U
Metribuzin(Lexone)	7.0U	7.0U	7.0U	7.0U
Chlorpyrifos(Dursban)	3.0U	3.0U	-	-
Fenthion(Baytex)	3.0U	3.0U	3.0U	3.0U
Tetrachlorvinphos(Stirophos)	2.0U	2.0U	-	-
Fensulfothion(Desanit)	2.0U	2.0U	2.0U	2.0U
Hexazinone(Velpar)	4.0U	4.0U	4.0U	4.0U
Coumaphos	2.0U	2.0U	2.0U	2.0U
Alachlor	20.0U	20.0U	20.0U	20.0U

Appendix 3. Continued

Part B1. Organophosphorus surrogate recoveries and matrix spike/matrix spike duplicate results. (sediment)

Surrogate Recovery

Bendiocarb	43%	42%	45%	42%

Matrix Spike Recoveries

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	MS Conc. (ug/Kg)	MS % Recovery
EPTC	90	0	99	110
Diazionon	45	0	31	69
Chlopyrifos	113	0	97	86
Tetrachlorvinphos	225	0	167	74

Matrix Spike Duplicate Recoveries

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	MSD % Recovery	% RPD
EPTC	80	90	112	1.8
Diazionon	40	27	68	1.5
Chlopyrifos	100	86	86	0.0
Tetrachlorvinphos	200	146	73	1.4

U - Indicates compound was analyzed for but not detected at the given detection limit.
MS - Matrix Spike
MSD - Matrix Spike Duplicate
RPD - Relative Percent Difference

Appendix 3. Continued

Part C. Results (ug/Kg) for base/neutral and acid compound in sediment samples collected as part of the 1989 BWMP.

Compound	Spokane R	Crab Ck	MS	MSD
Phenol	150 U	170 U	-	-
bis(2-Chloroethyl)Ether	74 U	83 U	81 U	80 U
2-Chlorophenol	74 U	83 U	-	-
1,3-Dichlorobenzene	74 U	83 U	81 U	80 U
1,4-Dichlorobenzene	74 U	83 U	-	-
Benzyl Alcohol	370 U	420 U	400 U	400 U
1,2-Dichlorobenzene	74 U	83 U	81 U	80 U
2-Methylphenol	74 U	83 U	81 U	80 U
bis(2-chloroisopropyl)Ether	74 U	83 U	81 U	80 U
4-Methylphenol	74 U	83 U	81 U	80 U
N-Nitroso-Di-n-Propylamine	74 U	83 U	-	-
Hexachloroethane	150 U	170 U	160 U	160 U
Nitrobenzene	74 U	83 U	81 U	80 U
Isophorone	74 U	83 U	81 U	80 U
2-Nitrophenol	370 U	420 U	400 U	400 U
2,4-Dimethylphenol	150 U	170 U	160 U	160 U
Benzoic Acid	740 U	830 U	810 U	800 U
bis(2-chloroethoxy)Methane	74 U	83 U	81 U	80 U
2,4-Dichlorophenol	220 U	250 U	240 U	240 U
1,2,4-Trichlorobenzene	74 U	83 U	-	-
Naphthalene	74 U	83 U	81 U	80 U
4-Chloroaniline	220 U	250 U	240 U	240 U
Hexachlorobutadiene	150 U	170 U	160 U	160 U
4-Chloro-3-Methylphenol	150 U	170 U	-	-
2-Methylnaphthalene	74 U	83 U	81 U	80 U
Hexachlorocyclopentadiene	370 U	420 U	400 U	400 U
2,4,6-Trichlorophenol	370 U	420 U	400 U	400 U
2,4,5-Trichlorophenol	370 U	420 U	400 U	400 U
2-Chloronaphthalene	74 U	83 U	81 U	80 U
2-Nitroaniline	370 U	420 U	400 U	400 U
Dimethyl Phthalate	74 U	83 U	81 U	80 U
Acenaphthylene	74 U	83 U	81 U	80 U
3-Nitroaniline	370 U	420 U	400 U	400 U
Acenaphthene	74 U	83 U	-	-
2,4-Dinitrophenol	740 U	830 U	810 U	800 U
4-Nitrophenol	370 U	420 U	-	-
Dibenzofuran	74 U	83 U	81 U	80 U
2,4-Dinitrotoluene	370 U	420 U	-	-
2,6-Dinitrotoluene	370 U	420 U	400 U	400 U
Diethylphthalate	74 U	83 U	81 U	80 U

Appendix 3. Part C Continued.

Compound	Spokane R.	Crab Ck.	MS	MSD
4-Chlorophenyl-phenylether	74 U	83 U	81 U	80 U
Fluorene	74 U	83 U	81 U	80 U
4-Nitrianiline	370 U	420 U	400 U	400 U
4,6-Dinitro-2-Methylphenol	740 U	830 U	810 U	800 U
N-Nitrosodiphenylamine(1)	74 U	83 U	81 U	80 U
4-Bromophenyl-phenylether	74 U	83 U	81 U	80 U
Hexachlorobenzene	74 U	83 U	81 U	80 U
Pentachlorophenol	370 U	420 U	-	-
Phenanthene	74 U	83 U	81 U	80 U
Anthracene	74 U	83 U	81 U	80 U
Di-n-Butylphthalate	74 U	83 U	81 U	80 U
Fluoranthene	30 M	83 U	26 M	37 M
Pyrene	74 U	100	-	-
Butylbenzylphthalate	74 U	83 U	81 U	150
3,3'-Dichlorobenzidine	370 U	420 U	400 U	400 U
Benzo(a)Anthracene	74 U	83 U	81 U	80 U
bis(2-Ethylhexyl)Phthalate	44 M	83 U	51 M	92 M
Chrysene	74 U	83 U	81 U	80 U
Di-n-Octyl Phthalate	74 U	83 U	81 U	80 U
Benzo(b)Fluoranthene	74 U	83 U	81 U	80 U
Benzo(k)Fluoranthene	74 U	83 U	81 U	80 U
Benzo(a)Pyrene	74 U	83 U	81 U	80 U
Indeno(1,2,3-cd)Pyrene	74 U	83 U	81 U	80 U
Dibenz(a,h)Anthracene	74 U	83 U	81 U	80 U
Benzo(ghi)Perylene	74 U	83 U	8 U	80 U
Dodecanamide	420 J	730 J		
Hexadecanoic Acid	1,300 J	1,500 J		

Part C1. Base/neutral surrogate recoveries and matrix/matrix spike duplicate results (sediment).

Base/Neutral Recoveries				
d5-Nitrobenzene	63.3%	65.1%	65.1%	62.1%
2-Fluorobiphenyl	80.6%	79.8%	79.8%	77.5%
d14-p-Terphenyl	77.5%	65.9%	65.9%	67.7%
Acid Recoveries				
d5-Phenol	77.4%	101.0%	79.5%	85.9%
2-Fluorophenol	74.7%	110.0%	98.0%	107.0%
2,4,6-Tribromophenol	41.1%	59.8%	50.7%	57.2%

(1) = Cannot be separated from diphenylamine.
U = Detection Limit
M = Indicates an estimated value of analyte found and confirmed by analyst but with low spectral match parameter.
MS = Matrix Spike
MSD = Matrix Spike Duplicate
J = Estimated value

Appendix 3. Part C1 Continued.

Matrix spike

Compound	Spike Added ug/Kg	Sample Conc. ug/Kg	MS Conc. ug/Kg	MS% Recovery	QC limit Recovery
Phenol	8000	0.0	6800	85.0	26-90
2-Chlorophenol	8000	0.0	7000	87.5	25-102
1,4-Dichlorobenzene	4000	0.0	3400	85.0	28-104
N-Nitroso-Di-n-Propylamine	4000	0.0	4200	105	41-126
1,2,4-Trichlorobenzene	4000	0.0	3900	97.5	38-107
4-Chloro-3-Methylphenol	8000	0.0	6800	85.0	26-103
Acenaphthene	4000	0.0	3100	77.5	31-137
4-Nitrophenol	8000	0.0	5700	71.3	11-114
2,4-Dinitrotoluene	4000	0.0	3200	80.0	28-89
Pentachlorophenol	8000	0.0	1700	21.3	17-109
Pyrene	4000	0.0	2900	72.5	35-142

Matrix spike duplicate

Compound	Spike Added ug/Kg	Sample Conc. ug/Kg	MSD% Recovery	% RPD	QC RPD	Limit
Phenol	8000	7500	93.8*	10	35	26-90
2-Chlorophenol	8000	7700	96.3	10	50	25-102
1,4-Dichlorobenzene	4000	3800	95.0	11	27	28-104
N-Nitroso-Di-n-Prop	4000	4400	110	4.7	38	41-126
1,2,4-Trichlorobenzene	4000	3900	97.5	0.0	23	38-107
4-Chloro-3-Methylphenol	8000	7200	90.0	5.7	33	26-103
Acenaphthene	4000	3200	80.0	3.2	19	31-137
4-Nitrophenol	8000	6100	76.3	7.0	50	11-114
2,4-Dinitrotoluene	4000	3400	85.0	6.1	47	28-89
Pentachlorophenol	8000	1800	22.5	5.7	47	17-109
Pyrene	4000	3000	75.0	3.4	36	35-142

* Outside control limits.

Appendix 3. Continued.

Part D. Results (ug/Kg) for herbicides on sediment samples collected as part of the 1989 BWMP.

Compound	Spokane R.	Crab Ck.	MS	MSD
Silvex (2,4,5-TP)	0.5 U	0.5 U	-	-
2,4,5-T	0.6 U	0.6 U	0.6 U	0.6U
Dinoseb	0.5 U	0.5 U	-	-
Dicamba	0.5 U	0.5 U	0.5 U	0.5 U
2,4-D	1.1 U	1.1 U	1.1 U	1.1 U
2,4-DB	5.5 U	5.5 U	5.5 U	5.5 U
Dalapon	40.0 U	40.0 U	40.0 U	40.0 U
MCPP	340.0 U	340.0 U	340.0 U	340.0 U

Part D1. Surrogate recoveries and matrix spike/matrix spike duplicate results for herbicides.

Surrogate Recovery	106%	81%	88%	84%

Matrix Spike Recovery

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	MS Conc. (ug/Kg)	MS % Recovery
Silvex	6.9	0.0	4.0	58.0
Dinoseb	14.0	0.0	4.9	35.0

Matrix Spike Duplicate Recovery

Compound	Spike Added (ug/Kg)	Sample Conc. (ug/Kg)	MSD Conc. (ug/Kg)	MSD % Recovery	% RPD
Silvex	6.8	0.0	4.3	63.0	8.3
Dinoseb	14.0	0.0	6.9	50.0	35.0

Appendix 4. Quality assurance results and discussion for metals analysis on fish tissue composites collected as part of the 1989 BWMP.

A review of this QA data indicates the laboratory did not meet one or more of the QA requirements for all metals, except selenium. Chromium, copper, and zinc were detected in the method blank; and data that is less than ten times the concentration found in the method blank will be flagged with a "B" qualifier code. Field replicate results show some variability that may be due in part to the difference in size of the individual fish that made up the composite (see Table 1). The laboratory duplicate results all are within 20% relative percent difference with the exception of one chromium value, which may have been affected by previously described QA problems. All metals except copper and zinc were outside the recommended tolerance limits for the Dogfish muscle DORM-1 reference material. Cadmium, chromium and lead also showed some Matrix Spike and Matrix Spike Duplicate results outside the exceptable ranges. Lead and chromium results appeared to be the most affected and are flagged with a "J" qualifier code indicating those values are estimates.

Part A. Laboratory results and acceptable ranges for the National Research Council Canada reference material DORM-1 dogfish muscle.

Analyte	Laboratory Results	Certified Value	Recovery	Control Limits	Outside Control
Arsenic	13700	17700 ± 2100	77.40	80-120	Y
Cadmium	50	86 ± 12	58.10	80-120	Y
	110	86 ± 12	123.30	80-120	Y
Chromium	6900	3600 ± 400	191.70	80-120	Y
	2000	3600 ± 400	55.60	80-120	Y
Copper	6100	5220 ± 330	116.90	80-120	
Lead	200	400 ± 120	50	80-120	Y
	750	400 ± 120	187.50	80-120	Y
Zinc	18300	21300 ± 1000	85.90	80-120	
Mercury	510	798 ± 74	63.90	80-120	Y

Appendix 4. Continued.

Part B. Matrix spike/matrix spike duplicate results for metals analysis on the 1989 BWMP fish tissue composites.

Analyte	Sample	Matrix Spike	Spike Added	% Recovery	Control Limit	Outside Control
Arsenic	0	1.30	1.57	82.80	75 - 125	
	0	1.31	1.59	82.40	75 - 125	
	0	1.51	1.55	97.40	75 - 125	
	0	1.36	1.56	87.80	75 - 125	
Cadmium	0.04	0.24	0.20	100	75 - 125	
	0.09	0.18	0.09	103.40	75 - 125	
	0.09	0.17	0.09	81.80	75 - 125	
	0.04	0.25	0.20	104.50	75 - 125	
	0.19	0.22	0.19	55.90	75 - 125	Y
	0	0.08	0.09	96.60	75 - 125	
	0.19	0.20	0.20	5.22	75 - 125	Y
Chromium	0.25	1.81	0.79	198.50	75 - 125	Y
	0.51	1.43	0.35	263.60	75 - 125	Y
	0.51	1.22	0.35	201.70	75 - 125	Y
	0.25	1.33	0.79	136.20	75 - 125	Y
	3.27	7.50	3.49	121.30	75 - 125	
Copper	0.93	10.90	9.83	101.40	75 - 125	
	0.93	10.80	9.91	99.60	75 - 125	
	0.27	9.93	9.68	99.80	75 - 125	
	0.27	10.10	9.77	100.60	75 - 125	
Lead	0.06	0.77	0.79	90.30	75 - 125	
	0	0.28	0.35	80.20	75 - 125	
	0	0.46	0.35	130.70	75 - 125	Y
	0.06	0.52	0.79	58	75 - 125	Y
	0	0.34	0.35	97.40	75 - 125	
Zinc	22.60	39.20	19.70	84.30	75 - 125	
	22.60	39.80	19.80	86.90	75 - 125	
	15.30	33.20	19.40	92.30	75 - 125	
	15.30	33	19.50	90.80	75 - 125	
Selenium	0	1.90	1.94	97.90	75 - 125	
	0	2	1.95	94.70	75 - 125	
Mercury	15.30	33.20	19.40	92.30	75 - 125	
	0.12	0.21	0.10	94.70	75 - 125	
	0.07	0.09	0.07	28.60	75 - 125	Y

Appendix 4. Part B Continued.

Analyte	Original Sample	Matrix Duplicate	RPD Limits	Control Limit	Outside Control
Arsenic	1.3	1.31	0.8	+ 20 %	
	1.51	1.37	9.7	+ 20 %	
Cadmium	0.24	0.25	4.1	+ 20 %	
	0.217	0.203	6.7	+ 20 %	
	0.184	0.166	10.3	+ 20 %	
	0.11	0.084	26.8	+ 20 %	Y
Chromium	1.81	1.33	30.6	+ 20 %	Y
	3.21	2.93	9.1	+ 20 %	
	1.43	1.22	15.8	+ 20 %	
	7.9	7.5	5.2	+ 20 %	
Copper	10.9	10.8	0.9	+ 20 %	
	9.93	10.1	1.7	+ 20 %	
Lead	0.77	0.52	38.8	+ 20 %	Y
	1.41	1.06	28.3	+ 20 %	Y
	0.28	0.46	48.6	+ 20 %	Y
	0.48	0.34	34.1	+ 20 %	Y
Zinc	39.2	39.8	1.5	+ 20 %	
	33.2	33.0	0.6	+ 20 %	
Selenium	1.9	2.0	5.1	+ 20 %	
Mercury	0.21	0.21	0.0	+ 20 %	
	0.07	0.07	0.0	+ 20 %	

Appendix 5. Quality assurance results for metals analysis on sediment composites collected as part of the 1989 BWMP.

The QA results show blank contamination for aluminum, copper, lead, and zinc; but all sample results are greater than ten times the blank concentration, so the data is not flagged. Matrix spike recoveries and duplicate results for arsenic were both outside the acceptable range. The data is flagged with a "J" and should be used only as estimated values. The results for the Buffalo River sediment reference material show low recovery levels for aluminum, antimony, chromium, and thallium, therefore, this data is also flagged with a "J."

Metals results (ug/Kg, dry weight) for the 1989 BWMP sediment composites.

		Al	Sb	As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Se	Ag	Tl	Zn
Buffalo River Sed.		16600000	1800	20100	NA	3600	86700	93200	153000	1340	39000	NA	NA	700	394000
	Certified	61000000	3790	23400	NA	3450	135000	98600	161000	1440	44100	NA	NA	1200	438000
	Value	+1600000	+150	+800		220	+5000	+5000	+17000	+70	+300			+200	+12000
	% Recovery	27.2	47.5	85.9	NA	104.3	64.2	94.5	95	93.1	88.4	NA	NA	58.3	90

NA - Not Analyzed